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The Spontaneous
Combustion of Coal

Chemical Engineering

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THE SPONTANEOUS COMBUSTION OF COAL

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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INTRODUCTION.

It has been said that the coal trade is considered one of the best indices of commercial progress of the United States and from an examination of the following data it is seen how great the coal industry has become. Virtually complete returns, compiled by Ed W. Parker, (1) statistician in charge of the division of mineral resources, U. S. Geol. Sur., show that the production of coal in the United States for 1907, not only far exceeded any previous record, but also exceeded by a considerable amount, all estimates of the output for that year.

The aggregate production of anthracite and bituminous coal for 1907 amounted to 480,450,042 net tons, valued at \$614,831,549.00 against 414,157,278 tons valued at \$513,079,809.00 for 1906, and a valuation of \$476,756,963.00 for 1905.

The increase in production in 1907 over 1906 was 66,292,764 net tons or 16.01% in quantity, and \$101,751,740 or 19.83% in value.

The production of bituminous coal in 1907 (2) amounted to 79.3% of the total production of coal and its value was 70% of the total value of all coal mined.

It is evident that this tremendous production of coal can not take place so as to fit the vagaries of daily demand.

In order to procure and maintain the most economic production of coal a uniform daily output is necessary, both from the point of view of the mine operators and the miner.

To guard themselves against unknown and unforeseen conditions such as labor difficulties, variations in output or delay in transportation, the large manufacturing interests are beginning to

see the need of supplying themselves with large amounts of reserve fuel.

Variations due to seasonable demands of fuel for domestic purposes necessitate the storage of coal either by the mining interests or the coal dealers. In the maritime world the storage of coal is one of the great problems of today. When it is remembered that our large battle ships and ocean greyhounds use upwards of 500 tons of coal a day the significance of the storage problem is at once apparent. For naval and merchant marine purposes coal must not only be stored on shipboard but large reserve supplies must be on hand at the various supply stations.

Wherever large quantities of bituminous coal are stored (and bituminous coal furnishes by far the greatest part of the energy used at the present day) the danger arising from spontaneous combustion is always at hand. It is not at all to be wondered at therefore that elaborate and costly measures have been taken to avert this hidden peril.

The U. S. government which uses upwards of a quarter of a million tons of coal yearly for the navy alone, has taken great precautions to avert the danger of spontaneous combustion in its new coal pile at Bradford on Narragansett Bay near Newport. There are about 60,000 tons of coal stored.

The coal bins or pockets are provided with temperature tubes, so that if incipient heating should occur it will be discovered and located long before a temperature has been reached at which combustion commences. These tubes consist of lengths of 4" galvanized pipe about 20 ft. long set in the bin floors and projecting upwards through the coal pile. They contain thermostats which

are arranged to indicate temperatures in excess of 150°F. Circuits are run from the 232 tubes to a general annunciator in the superintendent's office, so that if heating does occur an alarm is at once sounded and the exact position of the pile where the heating has developed is shown on the indicator.

The temperature of 150°F was decided upon as the danger point as the result of numerous experiments by the Navy Department which indicated that if the temperature of the coal reaches this point the increase in temperature beyond is very rapid.(3) At the New York Navy Yard compartments of 525 gross tons capacity have been built. The floors of these bins are of Portland cement and the side walls are made of a mixture of Portland cement, sand, and anthracite boiler cinders. The roofs are of iron. (4)

The danger of spontaneous combustion on shipboard is even greater than during ordinary storage, for the coal is usually stored in whatever space is unoccupied by other materials and this space is usually at the side of the vessel between the boiler rooms and the side planking. Here the coal is subjected to the heat of the boiler and engine rooms and is especially prone to spontaneously ignite.

Thus the danger arising from the spontaneous combustion of coal while in storage is readily seen, and is rapidly being recognized as the great problem in the storage of bituminous coals. Up to the present time some work and considerable theorizing regarding the nature and cause of spontaneous combustion has been done, but the views presented have been very contradictory as will be seen in the following chapter. The subject of spontaneous ignition and combustion is so closely allied to that of storage of coal, that it is thought that investigations in the latter phase of the subject

should be included, in the following researches and theories of those who have studied this problem.

HISTORICAL.

In 1865 (5) Varrentrapp reviews(6) Grundmann's work of 1862, in which the latter found that after exposing a Silesian coal in a pile of some 300 tons that a loss of 58.2 percent of volatile matter took place. Other workers later could not duplicate his work and ascribed the errors of Grundmann to poor sampling. Varrentrapp found from his experiments that on storing coal the oxidation of fresh coal is very rapid, and within the heap leads to a rise in temperature, which however, is very far from the ignition point. He states, however, that temperatures reaching the ignition point and causing combustion have at times been found.

L.Thompson(7) in 1865 found that dry coal in storage for six months lost $1/13$ of its calorific value, if however, the coal was moist the loss was much greater. He divides the weathering of bituminous coals into two classes known as "Dry rot" and "Wet rot". The latter he considers to be a sort of fermentation in which a part of the hydrogen escapes and some of the carbon is oxidized to carbon dioxide, in this way the coal loses calorific value in two directions.

Reder in 1866 (8) found that storing coal for a year caused a deterioration in the heating value, but no appreciable loss of weight.

Grundmann (9) found that while the coals lost gaseous constituents they gained in hygroscopic moisture and so the specific gravity of the coal remained constant. He also states that large pieces weather less than fine coal, and that rain and increased temperatures accelerate the weathering.

Fleck in 1865 (10) examined a series of six Saxon coals which had been preserved in a cabinet since 1856. The results of

his examination were then compared with analyses made nine years previous, when, it is presumed, the coals were in a fresh state. After such an exposure in a dry place three of the number, it was inferred, showed an important increase in proportion of ashes together with a corresponding decrease of organic matter, while the ashes of the remaining three appeared to have decreased. The explanation of such unlike results was sought by Fleck in the lack of uniformity of the related samples, especially as to the ratio of ashes. An increase of oxygen and of indisposable hydrogen was observed in each case, together with a loss of carbon and of disposable hydrogen. Hence the conclusion that at ordinary temperatures bituminous coal sustains a loss in carbon and of disposable hydrogen, and proportionately a loss in calorific value, which is increased in proportion to the addition of combined water.

The most careful of the early experiments made on this subject were those of Dr. Richter (11) in 1868 to 1870. He concluded that the weathering of coal is due to the absorption of oxygen, a part of which goes to the oxidation of carbon and of hydrogen in the coal, and part is taken into the composition of the coal itself; that if the heap becomes warm, either through this process or through any other cause, the action is accelerated, but then falls off, and becomes so slow that the changes effected within a year become difficult to estimate; that moisture, as such, has no direct influence upon the process, apart from the presence of pyrites or from the coal crumbling down more rapidly when wet than when dry, and therefore more rapidly heating up; that if the temperature does not go beyond certain limits (338° to 374°F) there is no appreciable loss of weight, but rather, on the whole, a gain, through the absorption

of oxygen. Also that it is not necessary to explain the loss in heating value, of coking power, and of gas yield by any theory of new arrangements of atoms, for it is sufficient to look at the absolute loss of carbon and hydrogen, and the increase in the proportion of oxygen. At a later date he concluded that large coal was affected less than small, not because it had less surface, but because small coal was a more active absorbent of oxygen and, therefore became more rapidly heated; that air-ways in a heap would have to be very numerous in order to prevent any rise in temperature, and that the heap ought to be so constructed as not to allow air to get from the air-ways into the bulk of the coal.

Haedicke in 1880 (12) assigned to pyrites, the leading part in spontaneous ignition but stated that it will not cause this unless the temperature is allowed to rise sufficiently.

Professor Fischer (13) of Göttingen, in his work on this subject prior to 1901 concludes that storage depreciation and spontaneous ignition are phenomena of oxidation; the part which is played by iron sulphide is disputed, but the variances which have given rise to the uncertainty are due to the differences between the different sulphides of iron present in coal. He claims that marcasite, for example, is much more weatherable than ordinary pyrite. Actual wetting is much more promotive of oxidation of the iron sulphide than heating in dry or even moist air. Besides this, Fischer finds that many coals contain sulphur in the form of unsaturated organic compounds. He finds that those coals which rapidly absorb bromine are those which are most liable to rapid oxidation and spontaneous ignition; and as a practical test he recommends shaking a gram of the finely powdered coal with 20 c.c. of a half-normal

solution of bromine for five minutes. Then if the smell of bromine has not disappeared the coal may safely be put in store; if it has it should be used up as soon as possible. The absorption of oxygen by the unsaturated organic compounds referred to is accompanied by a gain in weight and at the same time by a rise in temperature; and the warmer the mass the more rapidly does the oxidation go on, so that the temperature is apt to rise to a dangerous extent. Concurrently with the oxidation of these products we have oxidation of another set of organic compounds with evolution of carbon dioxide and water vapor, and this results, not in a gain, but in a loss of weight. Whether the mass as a whole gains or loses weight is therefore a question of the composition of the coal; but the loss in weight is in no case great. Covering wet slack coal with other coal is apt to produce spontaneous ignition; the danger here appears to arise from the sulphide of iron rather than from the organic compounds. Fischer regards ventilation of the coal heap with suspicion, not because the idea is in itself a wrong one, but because it is not practicable to ventilate the whole heap efficiently. He claims that the coal should be stored dry and kept dry under cover, and in layers not too deep.

In a paper read before the German Gas Association in 1900, Herr Schren, (14) Manager at Bonn, stated that it is no longer possible for many reasons, to work gasworks with a supply of coal renewed from month to month; and all questions affecting storage have therefore a continuously increasing importance. Undoubtedly there is a greater or less depreciation in quality of coal kept in store; and the causes of this have attracted a good deal of attention, though on the whole, it is surprising to find to how great an extent

the study of the chemistry of coal has been neglected. Questions of this nature assumed importance in connection with the spontaneous ignition of cargoes of coal in ships; in 1874, out of a list of 4,485 coal-laden ships no fewer than 60 caught on fire.

In a paper read by Prof. Vivian B. Lewes (15) at the 31st Session of the Institution of Naval Architects held at the Society of Arts, Adelphi, the author began by referring to the appointment of a Royal Commission in 1875 on the proposition of the Board of Trade and a Committee of Lloyds, to investigate the causes of the spontaneous ignition of coal cargoes, which had entailed serious loss of life and destruction of property. The Commission was assisted by Dr. Percy and Sir Fred Abel.

From 1875 to 1883 no less than 57 coal laden vessels were known to have been lost, while during the same period 328 were missing from unknown causes, though probably a large proportion of these losses were due to spontaneous combustion. In view of this fact it was suggested to the author that an inquiry into the causes and possible prevention of this serious evil was greatly needed in the Royal Navy as well as in the merchant service; and therefore he undertook it, and laid the results before the members of the Institute.

The author proceeded to point out that, besides the carbon and hydrocarbons coal contains certain mineral substances, as sulphate of lime or gypsum, silica, and alumina, while in nearly all kinds there is to be found disulphide of iron, "brasses" or pyrites. Of these constituents, those that are likely to produce heat and cause spontaneous ignition, in newly won coal, are the carbon, hydrocarbons, and brasses, which when they come into contact with air and

moisture, give rise to certain chemical actions. He then described at length the influence of each of these substances in the production of heat. Taking carbon first, he remarked that it is one of those substances which possess to an extraordinary degree, the power of attracting and condensing gases upon their surfaces - the power varying with the state of division and density of the particular form of carbon used. In the case of newly-won coals, the least absorptive would, he said, take up 1 and 1/4 times, while others would absorb three times their own volume of oxygen. This absorption is very rapid at first, but gradually decreases; and it is influenced to a very great extent by temperature. Air-dried coal absorbs oxygen more quickly than wet coal.

Dealing in the next place with the action of the bituminous constituents of coal in causing spontaneous ignition, the author explained that all coal contains a certain percentage of hydrogen, which is in combination with some of the carbon, and also with the nitrogen and oxygen, and forms with them the volatile matter in the coal. The amount present in this condition varies very largely; being very small in anthracite and very great in cannel and shale. When the carbon of the coal absorbs oxygen, the compressed gas becomes very chemically active, and soon commences to combine with the carbon and hydrogen of the bituminous portions, converting them into carbon dioxide and water. This chemical activity increases rapidly with rise of temperature; so that the heat generated by the absorption of the oxygen causes the latter to rapidly enter into chemical combination. Chemical combination of this kind--i.e., oxidation- is always accompanied by evolution of heat; and this further rise of temperature again increases rapidity of oxidation, so that a steady

rise of temperature is set up. This taking place in the centre of a heap of small coal, which, from the air and other gases enclosed in its interstices, is an admirable non-conductor of heat, will often cause such heating of the mass that if air can percolate slowly into the heap in sufficient quantity to supply the necessary percentage of oxygen for the continuance of the action, the igniting-point of the coal would be soon reached. It has been suggested that very bituminous coal (such as cannel, shale, and coals containing schist) is liable to spontaneous ignition from the fact that a rise in temperature would cause heavy oils to exude from them, which, by undergoing oxidation, might cause rapid heating. Experiment, however, not only shows that this is not the case, but that the heavy mineral oils have a remarkable influence in retarding heating.

The action of iron disulphide, pyrites, or "brasses," in promoting spontaneous ignition, was next discussed. The author said that ever since Berzelius first expressed the opinion that the heat given out by the oxidation of iron disulphide into sulphates of iron might have an important bearing on the heating and ignition of coal, it had been adopted as the popular explanation of that phenomenon; and although the work of Richters clearly proved this not to be the case, the old explanation was still given. Dr. Percy, in 1864, pointed out that probably oxidation of the coal had also something to do with spontaneous combustion - a prediction amply verified by Richter's researches some six years later. This disulphide of iron was found in coal in several different forms - sometimes as a dark powder distributed throughout the mass of the coal, and scarcely to be distinguished from coal itself. In larger quantities it often thin golden-looking layers in the cleavage of the coal, whilst it

sometimes occurred as large masses and veins, often from 1 in. to 2 in. in thickness; but inasmuch as these masses of pyrites were very heavy, they rarely found their way into the screened coal for shipment, many hundreds of tons of these brases being annually picked out from the coal at the pit's mouth, and utilised in various manufacturing processes. When the air was dry, the pyrites underwent but little change at ordinary temperatures. In moist air, however, they rapidly oxidised when in a finely-divided condition- the first action being the formation of ferrous sulphate and sulphur dioxide, together with the liberation of sulphur; the relative amounts of the latter being regulated by the temperature and the supply of air, whilst longer contact with moist air converted the ferrous sulphate into a basic ferric sulphate generally termed "misy". It was during this process of oxidation that the heat supposed to cause the ignition was evolved. But when it was considered that some of the coals most prone to spontaneous combustion contained only 0.8 per cent of iron pyrites, and rarely more than 1.25 per cent, the absurdity of imagining this to be the only cause of ignition became manifest. If 100 lb. of coal were taken, and the whole of the pyrites in it concentrated in one spot and rapidly oxidized to sulphate, the temperature would barely be raised to 100°C if all loss of heat could be avoided. The author had carefully determined the igniting-points of various kinds of coal, and found them to be as follows:-

Cannel.....	698°F. = 370°C.
Hartlepool.....	766°F. = 408°C.
Lignite.....	842°F. = 450°C.
Welsh steam.....	$870\frac{1}{2}$ °F. = 477°C.

So that no stretch of imagination could endow the small trace of pyrites scattered through a large mass of coal, and undergoing slow oxidation, with the power of reaching the needful temperature. Richters fully realised this point, and discarded the idea of the pyrites doing anything more than adding their mite to the causes which bring about rise of temperature. In this, however, Lewes thought Richters was mistaken, his own experiments pointing to the fact that they might increase the liability to ignition when present in large quantities, and do so by liberating sulphur under certain conditions. A still more important part played by the pyrites, is that as they become oxidised to ferrous sulphate they swell in size, and so tend to split up the coal into small pieces, and, by exposing a large extent of fresh surface to the air, cause increase of temperature and energetic chemical action.

The author, Lewes, then traced the actions which culminate in ignition. He said that on newly-won coal being brought to the mouth of the pit, it at once began, by virtue of its surface action, to absorb oxygen from the air. Unless piled in unusually large heaps and a good deal broken, it did not, however, as a rule, show signs of heating, as the exposed surface was comparatively small; and the air finding its way freely between the lumps, kept down the temperature. The coal was now screened, and the obtrusively large lumps of brasses picked out. It was then put into trucks, and enjoyed the disintegrating processes of joltings and shuntings innumerable - every jar adding to the percentage of small coal present, and a corresponding increase in the size of the surface exposed to the air. Arrived at the docks, it had to be transferred from the truck to the ship, which was done by one of the numerous forms of tips, shoots, or spouts

employed for the purpose; and it was during this operation that more harm was done than at any other period. The coal first shot into the vessel was, by reason of the distance which it had to fall, broken down into small lumps, and, having to bear the impact of the succeeding load falling upon it from a height, rapidly became powdered into slack; whilst the succeeding loads, falling in on the cone so formed became more or less broken down, so that by the time the cargo was all taken in, a dense mass of small coal was to be found under the hatchway. It was invariably at this point that heating took place, as the large surface exposed fresh to the air by the breaking down of the coal caused rapid absorption of oxygen, and consequent rise of temperature. This set up chemical combination between the oxygen absorbed by the coal and the hydrocarbons and coal "brasses." The combination of the "brasses" with oxygen caused the swelling of the oxidised mass, and the splitting up of the coal. Fresh surfaces were exposed, and more absorption of oxygen took place; and the igniting-point of the sulphur vapour and sulphur compounds distilled out of the pyrites was reached, and rapidly raised the temperature to the ignition-point of the coal. It was only, however, in cases where large quantities of dense coal brasses were present, that this action could occur. On examining the evidence to be obtained as to the conditions under which spontaneous ignition of coal ships usually takes place, Lewes found that the liability to such accidents increases with

- (1) the tonnage of the cargoes,
- (2) the ports to which shipments are made,
- (3) the kind of coal of which the cargo consists,
- (4) the size of the coal,

(5) the shipping of coal rich in pyrites while wet,

(6) the ventilation of the cargo, and

(7) the rise in temperature in steam colliers due to the introduction of triple-expansion engines and high-pressure boilers.

Having discussed the chemical and physical conditions which lead to the spontaneous ignition of coal, the author proceeded to formulate precautions tending to prevent such disasters. These had reference to the choice of coal for shipment to distant ports, and to the precautions to be taken during shipment and when the coal is on board. He advised that the coal should be as large, free from dust, and have as little "smalls" as practicable. It was better as free from pyrites as possible, in order to prevent disintegration after shipment; and it should contain, when air-dried, not more than 3 percent of moisture. No coal should, he said, be shipped to distant ports until at least a month had elapsed after it was brought to the surface at the pit's mouth. Every precaution should be taken to prevent the breaking up of the coal while being taken on board, and on no account should any accumulation of fine coal be allowed under the hatchways. When possible, the coal should be shipped dry, as external wet, by producing oxidation of the pyrites, caused disintegration. When the coal had all been taken in, it should be battened down, and the hatches not opened again until the vessel reached her destination; the only ventilation allowable being a 2-inch pipe just inserted into the crown of each coal compartment, and led 12 feet up the nearest mast - the top being left open. This would be quite sufficient to allow free egress to any gases evolved by the coals, but would not allow undue access of air. Into the body of the coal cargo itself would be screwed, at regular intervals of about 6 feet,

iron pipes, closed at the bottom, and containing electrical alarm thermometers, set at a certain temperature, the attainment of which would be indicated by the ringing of a bell, which would not cease until the temperature had again fallen, and then the spot in which the heating had taken place would be indicated by an index-board. The existence of overheating having been reported by the bell, and recorded by the index, the author offered suggestions for suppressing it. He advocated the injection of compressed carbonic acid gas, and explained his plan as follows:- The nozzle attached to the screw valve on the bottle of condensed gas would have a short metal nose-piece screwed on to it, the tube in which would be cast in solid, with an alloy of tin, lead, bismuth, and cadmium, which could be so made as to melt at exactly 200°F.(93°C.) . The valve would then be opened, and the steel bottle buried in the coal during the process of loading. The temperature at which the fusible metal plug would melt is well above the temperature which could be reached by any legitimate cause, and would mean that active heating was going on in the coal. Under these conditions, the pressure in the steel cylinder would have reached something like 1,700 lb.; and the moment the plug melted, the whole contents of the bottle would be blown out of it into the surrounding coal, producing a large zone of intense cold, and cooling the whole of the surrounding mass to a comparatively low temperature. The action, moreover, would not stop here, as the cold, heavy gas would remain for some time in contact with the coal - diffusion taking place but slowly through the small exit-pipe. When coal has absorbed as much oxygen as it can, it still retains the power of taking in a considerable volume of carbonic acid gas; and when coal has heated, and then been rapidly quenched, the amount of

gas so absorbed is very large indeed, and the inert gas so taken up remains in the pores of the coal, and prevents any further tendency to heating. Indeed, a coal which has once heated, if only to a slight degree, and has then cooled down, is perfectly harmless, and will not heat a second time. It is not by any means necessary to replace the whole of the air in the interstices of the coal with the gas, as a long series of experiments show that 60 percent of carbonic acid gas prevents the ignition of the pyrophoric substances. A hundred cubic feet of gas can be condensed in the liquid state in a steel cylinder 1 foot long and 3 inches in diameter; and it has been shown that a ton of coal contains air spaces equal to about 12 cubic feet. One of these cylinders would therefore have to be put in for every 8 tons of coal, and these would be distributed evenly through the cargo, and near the alarm thermometers, which would be set to ring a degree or two below the point at which the fusible plug would melt. The bell ringing in the captain's room would warn him heating was taking place, and the bell would continue to ring until the cylinder had discharged its contents, and had cooled down to a safe degree, so that the whole arrangement would be purely automatic, and yet the officers would know if everything was safe. If the precautions advocated were taken, no danger could arise until the arrival of the ship at her destination, and the commonest precautions would then suffice.

In conclusion, the author remarked that the question of preventing the heating and ignition of stores of coal on land and ready for use in bunkers, could not be met so well by the use of the liquid gas; and in these cases it would be found beneficial to dress the coals with a little tar or tar oil, which would close the pores,

and to a great extent prevent oxidation. He believed this was advocated by Lachman about 1870. Crude petroleum in small quantities for this purpose would also be found valuable, for it had no tendency to oxidise itself, and lowered the tendency in other bodies, besides coating them and so preventing access of oxygen.

In a later paper Professor Lewes (16) of the Royal Naval College says, in the spontaneous ignition of coal stored in bulk, the oxidation of the pyrites present, only plays a very subsidiary part, the chief factor being the surface condensation of the oxygen in the pores of the coal and the action of the condensed gas in effecting the oxidation of the hydrocarbons present in the coal. While sufficient ventilation to prevent any considerable increase in temperature within the mass is effective in preventing ignition it is practically impossible to maintain this condition in large coal stores or in a cargo on board ship, where usually only enough air enters to lead to dangerous heating. The recent suggestion to thoroughly wet the whole mass of coal is impracticable owing to the great increase of weight brought about if sufficient water is added so as to be effective, and too small a quantity of water only accentuates the danger.

The extinction of coal fires which break out on board ship is a matter of extreme difficulty, owing to the frequent impossibility of getting water to the exact seat of the fire and to the formation of hydrogen and carbon dioxide by the action of the steam on the incandescent fuel, which results in the production of an explosive mixture in the coal bunkers. In order to extinguish at an early stage any fire which may break out, the author recommends that small cylinders of liquid CO_2 should be buried in different parts of the mass of coal during loading.

A. O. Doane(17) in 1904 states that the amount of moisture present in a bituminous fuel after drying in the air, is stated to be a measure of the risk of spontaneous ignition when the fuel is stored; bituminous coals containing over 4.75% of moisture are dangerous. Coal bins should be of iron or steel protected by concrete, and should be roofed over. Free air passages should be provided around the walls and beneath the bins so as to keep them cool, and the depth of coal stored should not be over 12 feet. The customary method of providing air passages in the body of the fuel is useless, since it only tends to accelerate oxidation, and does not produce a sufficient current of air to keep the temperature down. Cracks or joints in the walls of the fuel bin increase the risk of spontaneous ignition for similar reasons.

Durand (18) has explained the spontaneous ignition of coal as being due to the presence of pyrites, which on oxidation under suitable conditions inflames, and then sets fire to the coal in which it is embedded. According to Fayol's experiments, however, the real cause of this phenomenon is the oxidation of the coal itself and not of the pyrites. The absorption of oxygen by coal takes place more or less readily according to the temperature and the coal being more or less finely divided. Lignite in the state of fine dust takes fire at 150°, gas carbon at 200°, coke at 250° and anthracite at 300° or above. On heating a mixture of finely powdered coal and pyrites up to 200° for four days the coal took up 6% of oxygen while the pyrites absorbed only 3.5%. Hence coal absorbs oxygen much more energetically than pyrite does, which has been confirmed by the following experiment. 900 gr. powdered coal and 3,350 grs. of powdered pyrites were placed in tin cans and put

in a drying chamber. Up to 135° both behaved similarly, but from there on the temperature of the pyrites remained almost stationary while that of the coal quickly rose, ignition taking place a few hours afterwards. Two other samples of coal and pyrites were put in a chamber at 200°. The temperature of the coal quickly increased. After 40 minutes it got up to 200°, and the coal took fire, while the pyrites had at the same time only been raised to 150°. The ignition of the coal was not at all hastened by an admixture of pyrites.

The United States Admiralty (19) has made experiments and gives valuable directions for preventing the spontaneous combustion of coal. Anthracite is excluded from the inquiry since only bituminous coals are liable to catch fire. The ignition of coals may be induced by condensation and absorption of the oxygen of the air by the coal, whereby the temperature is raised so high that chemical combination between the hydrogen and oxygen can take place. This easily happens if the coal be very pure and brittle, if the outside temperature be also high, and the necessary ventilation be wanting. Another cause of ignition is the action of moisture on the sulphur of many pyritic coals, not so much from the heat of the chemical reaction as from the circumstance that the coal is split and broken up, and so fitted for the absorption of oxygen.

The arrangements for preventing ignition on board ship are not taken up, but it is said that on land it is mostly the pyritic coals that take fire. Care should be taken that the coal is stored on iron floors, and covered, the height of the heap not to exceed 2 to 2-1/2 metres away. For sea voyages the coal should not be laden earlier than one month after it has been mined.

Mr. Stelkins, (21) in his report before the International Navigation Congress in 1902, stated that the tendency towards spontaneous ignition of coal increases with the height to which the coal is piled. Stacks higher than fifteen feet should not be made. Rain during and after stacking and compression caused by dumping coal from a great height on the stack, all add to the danger of ignition.

Mr. F. M. Griswold (22) of the Home Insurance Company, in 1904 states that spontaneous ignition is more marked in free burning or so-called "high steaming coals" including "gas coals". These coals usually contain a large amount of volatile matter and small amounts of oxygen. The tendency towards spontaneous ignition increases when sulphur or lignites are found in the coal and especially when pyrite is present. Slack, mine run, and dirty coal are dangerous because of the fine particles present, the latter gradually sift to the bottom and are compressed.

A satisfactory explanation of spontaneous ignition and combustion of bituminous coal has not as yet been made. The best authorities say it is due to chemical changes in the substance of the coal resulting from the absorptive powers of carbon, the latter increases with rise in temperature. Rise in temperature may be due to the chemical action caused by slow oxidation or to the mechanical force of pressure, both of these conditions may be stimulated by moisture and the presence of pyrites. Some claim that over 2-1/2 percent of sulphur in the form of pyrite is dangerous. Various tests have been proposed to determine the liability of a coal to heat, such as the gain in weight of the coal at 250°F. and the absorption of bromine, but these tests are not valuable as it is difficult to tell how much oxygen the coal has already absorbed. He

recommends that no wood be used in the construction of bins, that all iron-work be covered with concrete, that no steam pipes or flues be near the bins, that a good circulation of air be about the sides and under the bins, and that the coal should not be piled to a depth greater than twelve feet. He also recommends that the bins be roofed, and that they contain pipes in which thermostats should be placed, and when the latter register 140°F, something should be done to stop the rise in temperature.

A. E. Dixon (26) in 1906 says that spontaneous ignition occurs with friable bituminous coal, and particularly with those grades containing brasses or iron pyrites, and when the coal is damp the trouble is increased. The cause is probably due to the absorption of oxygen by the carbonaceous material, just as is the case with oily cotton waste.

An article describing the coal storage department of the works of the Lackawanna Steel Company (23) says, "derricks are used to pile the coal and they are able to pile it to a height of 60 feet but to avoid danger of spontaneous combustion, it was deemed advisable to restrict the height of the piles to 20 or 30 feet."

Mr. Peter Bullock (24) gives several cases of coal piles catching on fire, seemingly due to spontaneous combustion. In all, about ten or twelve cases were cited, about half of these cases he believes to be due to heating from steam pipes which were near by, for the others he gives no explanations.

Groves and Thorp (25) state that gases occluded in the crevices or cavities of the coal escape during mining and continue to do so after storage. The inflammable nature of these gases make them a source of great danger, for it is believed that they are the

causes of many of the disastrous explosions on board vessels carrying coal as a cargo.

Dennstedt and Bünz (20) in 1908, give the following conclusions:-

Self ignition increases in a ratio corresponding to the amount of moisture in air dry coal, mechanically combined moisture is not meant for the coals used gave the impression of being perfectly dry, the moisture seems to be water of constitution.

Surface absorption has the same degree of importance as the above water of constitution. The question certainly is not one of hygroscopicity, or of the hygroscopic inorganic salts present, for water soluble mineral salts are found in very small quantities in all coals, so small that they do not even increase the surface absorption.

Moisture and its reabsorption is allied to, or controlled to a certain extent by the organic substances and their composition. It may also be noticed here that the humic acids formed in the coals are exceedingly hygroscopic. But these cannot cause the surface absorption in the original coals because no completely formed humic acids are present therefore the increased surface absorption of the oxidized coals is undoubtedly due to the humic acids. The increasing Maumene number (with increasing self ignition) is also in accordance with the idea of water of constitution, and here it is also seen that the organic substances have an influence for the Maumene number increases in the same ratio even in those coals that were dried in a current of carbon dioxide. It is very remarkable that these coals, dried in this way, should cause a rise in temperature when they are stirred in cold water (this property increases as

self ignition increases). The Maumene number can therefore well serve as a standard which would decide a coals power of self ignition.

Neither amount nor kind of mineral substance or pyrite found in coal have any effect on the self ignition, this is seen without a doubt from a consideration of the analytical data. The pyrite content is very small, and besides the pyritic coals are not the easiest to self ignite. One could also think of certain catalytic actions, to this effect we made numerous observations upon coals which we were sure had caused fires, and they had only a very small amount of pyrite that occurred in a fine condition. This pyrite was found in the slaty portion of the coal and upon fresh cleavage fractures in the form of a fine sulfur colored film. But the fact that just such coals, which are very easily self ignitable such as Scotch coal No. 6 contained a minimum quantity of pyrite carries one away from the above idea. The same might be thought of the hydrochloric acid soluble iron in the original coal, that this might be due to a catalytic action but here also the amount is so small and does not grow with the degree of self ignition, that we did not even think it necessary to insert the analytical data in our tables. One could rather speak of the water soluble iron in the oxidized coal as due to this cause, sometimes in coals that have been stored for a long time and perhaps have become wet too, an oxidation of pyritic iron in the form of basic sulfate is found; but we did not find any increased self ignition in them.

From the above it seems to us without a doubt that the organic substances control the self ignition of coal, and it depends not so much on the amount but rather upon the kind and composition.

This follows directly from the ultimate analysis, of course organic combined sulphur and nitrogen have no effect at least the amount of the same. For it is seen that both are not found in any greater amounts in coals that are easily inflammable over coals not easily so. With the sulphur one could think of the formation of easily inflammable compounds, for example carbon bisulfid. During the oxidation process we have looked for carbon bisulfid but have not found even a trace. Very conspicuous in the elemental composition is the proportionately small amount of hydrogen in the more inflammable coals, and the particularly larger amount of oxygen which is especially noticeable in the small amount of available hydrogen.

If the self warming and ignition is caused by this oxidation, which we believe has been shown, then at first glance it seems as a contradiction that those coals already so rich in oxygen are the most easily oxidized. But when one thinks that all coals are finally striving for a similar or equal character or composition then one can easily picture that a transition period of marked inflammability exists, which the easily inflammable coals have already reached. This is in accordance with the remarkable properties of the coals in Class II, which with preparatory treatment at 135°C with oxygen become more easily inflammable. This point seemed to us to be of sufficient weight to cause certain quantitative experiments to be made so as to prove it. With coal No. II (Germania) a marked change takes place by treating with oxygen at 135°C. This change consists of an addition in weight and a considerable loss of carbon dioxide and water, and this we think proves our assertion. Of course it is not necessary in order to change to an inflammable coal that the above must take place throughout the entire coal. It

is sufficient if it happens in certain localities or perhaps only at the surface of small coal particles. That the addition in weight, which takes place in oxidation, caused by the taking up of oxygen, is not substantially less in the less inflammable coals, with the exception of the altogether unflammable coal marked Nixon Navigation, this rests clearly on similar reasons, the same is found under table 6, from the ultimate analysis of the oxidized coal showing the addition of oxygen and the loss of carbon and hydrogen. Altogether out of place in this respect is the unflammable coal No. 1, Nixon Navigation, which oxidizes very slowly.

The end product of the oxidation is clearly seen to be the humic acids and from the humic number is found without possibility of contradiction how the easily inflammable and oxidizable coals are far above the others. Less easy to account for is the fluctuating value or amount of pyridin extract especially when one sees the content of the original and oxidized coals, but one thing is certain that in the majority of cases the extract grows with the degree of self ignition and is increased by oxidation. The one exception is Coal No. II, which is perhaps ascribable to imperfect methods.

Our researches show that the organic parts of the coal play two different roles, which have little to do with one another. That portion soluble in organic solvents seems of similar character and composition and perhaps of similar origin as the soluble portion of Braunkohle for example the so called Montanwachs only the coal extract contains more oxygen and is therefore probably of similar origin but changed by oxidation.

That portion of the coal insoluble in organic solvents we look upon as the real coal substance probably formed from

cellulose in the original wood; and that substance is which on further oxidation yields the humic acids, and which although not altogether, still in the main part determines the self ignition of the coal. It contains also the unsaturated compounds upon which the iodine addition rests which in the iodine number express themselves quantitatively, they run parallel with the capacity for oxidation; the remarkable fluctuation of the iodine number in the original and oxidized coals we leave for the present purposely untouched.

But since the iodine number is so easy to determine, one has in the main, a practicable means next after the Maumene number of determining the degree of danger from fire of the coal. Our specially devised apparatus would be preferred to either method.

In conclusion the practical chemist will ask if it is possible through the addition of chemicals or certain methods of handling to take from the coals their property of self ignition, and we have worked in answer to this question and hope to be able to report over our efforts in this direction in the future.

SUMMARY OF OPINIONS.

Reviewing the literature given in the preceeding chapter it is seen that opinions differ as to the real cause of spontaneous combustion. The leading factors may, however, be summed up as being the following:-

- (1) The kind of coal, in regard to its volatile matter.
- (2) The purity of the coal.
- (3) The presence of pyrite or other sulphur compounds.
- (4) The temperature of the coal.
- (5) The size of the coal.
- (6) The presence of occluded gases in the coal.
- (7) The presence of moisture.
- (8) The accessibility of oxygen.
- (9) Pressure on the coal.

From the ignition temperatures given by Durand it is seen that only those coals (such as the lignites, bituminous, and semi-bituminous, containing large amounts of volatile matter) are liable to ignite spontaneously, and that anthracite with its very low percentage of volatile matter is practically entirely excluded. The work of our own Government seems to indicate that coals of exceptional purity are more apt to heat up than coals containing large amounts of extraneous matter. This is probably due to the fact that the very pure coals are able to condense and absorb the oxygen of the air much faster than other coals and so cause an increase in temperature which finally results in the chemical combination of the oxygen and the hydrogen occluded in the coal. This view is confirmed by the later work of Dennstedt and Bünz who found that those

coals causing spontaneous combustion or those coals which oxidized and increased in temperature most rapidly were remarkably free from mineral matter and pyrite.

As to what part sulphur compounds, pyrite especially, play in the spontaneous ignition of coal, opinions differ greatly. Some believe pyrites to be the leading factor, while others believe it plays no part at all, or if so, ascribe to it a position of minor importance and believe its action to be merely a subsidiary one. The oxidizing action of the air upon pyrites is however admitted, and the notion seems to be fairly general and well established that pyritic oxidation tends to raise the temperature of the coal. If this is true and if the initial rise in temperature of the coal heap is really due to pyritic oxidation, then the pyrite plays a very important role in the subject of spontaneous combustion, for it seems firmly established that if the coal once reaches a certain temperature an increase in temperature, whether due to oxidation or other causes, is sure to take place, with the final result being, combustion. Others, however, believe that the only influence of the pyrite is a mechanical one, in which the oxidation of the thin films of pyrite in the coal merely serve to break up the coal. This seems to be true to a certain extent, for seams of Illinois coal have been found in which the pyrite has almost completely oxidized to ferrous sulphate and in doing so has torn the coal into shreds.

Most of the authors agree that the temperature of the coal undoubtedly is one of the main factors in the whole subject of spontaneous combustion for cases of spontaneous combustion have occurred time and again where probably they never would have occurred if there had not been an initial heating in some way or other,

Numerous cases are on record where the cause of the spontaneous ignition of large coal stores was finally traced back to initial heating from flues or steam pipes. This increased temperature, whether coming from outside sources or from physical or chemical reactions within the coal tends to accelerate the absorption of oxygen and thereby increase the oxidation of the coal. It also tends to drive out the inflammable gases occluded in the coal and so greatly accentuates the danger of spontaneous ignition.

That fine coal is a more active absorbent of oxygen and more liable to ignite spontaneously than large coal, was shown as far back as 1868 by Richter. Practically all of the later experimenters in this field concede this to be true, for having a greater surface the fine particles can absorb much more oxygen than large lumps; and since this rapidity of absorption causes an increase in temperature, which in turn, produces favorable conditions for further absorption and for chemical-action between the oxygen of the air and the hydrogen of the coal, the danger of spontaneous combustion is greatly accentuated.

Throughout the literature warnings are found cautioning coal users and shippers against storing fine coal. Some have even advocated that only large lumps should be transported on shipboard and that these should be carefully packed by hand. The covering of coal piles with slack is to be avoided, also the coal should be handled as little as possible to avoid disintegration, for in handling the finer particles gradually sift down to the bottom of the pile where they accumulate and are a source of danger, for at the center and bottom of the pile the most favorable conditions for spontaneous ignition exist. here the coal is sufficiently insulated

by the surrounding coal so as to retain all the heat that is generated. Air is accessible in sufficient amounts so as to cause oxidation, and still is not present in large enough amounts to conduct away the heat. The fact that friable coals are more prone to ignite spontaneously than coals not so, also seems to substantiate the above opinion. Dennstedt and Bünz in their work on this subject even went so far as to make a friability test on all the coals they worked with, for they conceded the danger arising from the fine coal with its great avidity for oxygen, and recommended that they considered safe to transport on board ship, only those coals passing a certain standard in their friability test.

While it is now a well known fact that gases of an inflammable nature are occluded in coal, their relation to the spontaneous ignition of coal has not yet been clearly established. Whether the gases occluded in the coal are the real cause of spontaneous ignition is doubtful, but if the coal becomes heated up by oxidation or some other cause to a temperature high enough for the oxygen of the air to unite with these gases, then it is seen that the presence of these gases constitutes a source of danger and then coals with large amounts of gases occluded in them would be more liable to ignite than coals containing smaller amounts of these gases.

Opinions differ greatly as to what part the moisture in coal plays in the spontaneous ignition of the same. Some believe the moisture content of the air dry coal to be a direct index of its power to ignite spontaneously. Others think that the presence of moisture materially assists the pyritic oxidation, while others believe that the only part moisture plays is a mechanical one, where

the moisture by alternate freezing and thawing breaks up the coal into smaller particles and so exposes more surface to the oxygen of the air. There are many who believe that aside from increasing the pyritic oxidation, that moisture acts as a catalytic agent between the carbon and hydrogen of the coal and the oxygen of the air. This idea is substantiated to some extent by the fact that some coals containing minimum amounts of pyrite are never the less very liable to spontaneous ignition; and coals of this class, namely, the Scotch coals have been known to cause fires.

That the combination of oxygen with the constituents of the coal causes a rise in temperature seems to be firmly established. Which particular constituent is the cause of the rise in temperature has not, however, been shown with any great degree of certainty, although at present the idea is generally held that the combination of oxygen with the carbon and hydrogen of the coal is the cause of this increase in temperature. The presence of oxygen is therefore to be avoided and the old idea of thoroughly ventilating the coal piles by free access of air, is gradually being dropped, and at present authorities deem it advisable to keep the coal away from the air as much as possible. In marine transportation it is even advocated to seal the hatches and allow no air whatever to come in contact with the coal. If ventilation is used to lower the temperature of the coal it should be through pipes, so that the cooling air cannot come in contact with the coal at all.

The belief that pressure on the coal is one of the leading factors in the spontaneous ignition of coal, seems to be gaining ground, and because of this fact it is advocated that coal heaps should not be any higher than 20 feet. Also the practice of

dropping coal from great heights is to be avoided, because of the compression produced on the coal below.

EXPERIMENTAL INVESTIGATIONS.

From the summary at the close of the preceeding chapter it is seen that many factors influence, or determine to a certain extent the liability of a coal to ignite spontaneously. Some of the leading factors are, the presence of pyrite, the size of the coal, the temperature of the coal, and the presence of moisture.

The object of this investigation was to determine if possible how great an influence each of the above has in the spontaneous ignition and combustion of coal.

New Ohio, Carterville coal from Williamson county, Illinois, was used for this work, about one half ton of large lumps being required for the entire experiment. These lumps were ground up to the requisite sizes as needed. The grinding was done in a small "Chipmunk" crusher and the ground coal was then run through a revolving screen whereby it was sized. The screen was a hollow drum of sheet iron about six feet long in which holes of the following sizes were drilled: $1/8"$, $1/4"$, $3/8"$, $1/2"$, $3/4"$, and $1"$. The coal coming through the $1/4"$ holes, known as size $1/8 - 1/4$, was always screened twice because a small amount of dust escaped the $1/8"$ holes the first time, so to make the $1/8 - 1/4$ size dust free it was screened twice. Each time only enough coal was ground and screened to meet immediate demands and any left over was thrown away so that the coal used was always fresh and unoxidized.

Since the influence of the temperature of the coal was to be determined the coals were placed in constant temperature ovens for a period of three days each. The following temperatures

were maintained in four different ovens, 40°, 60°, 80°, 115°, Centigrade. The coal was first placed in the 40° oven and after a period of three days was moved up to the 60° oven, after another period of three days it was moved to the 80° oven, and finally after another period of three days it was moved to the 115° oven, and, after remaining in this oven for three days the coal was removed. A five gallon stone jar having the bottom perforated with 1/2 inch holes was used as a container for the coal. A jar of this size held a sample of coal weighing about 35 or 40 pounds.

The ovens were constructed as follows: they consisted of two wooden boxes one set inside of the other. The boxes were in the form of cubes, the outer box being a three foot cube made of 1 1/8" pine boards and the inner box was also in the form of a cube made of the same material only it was eight inches smaller than the outside box. This left a space of four inches on all sides between the two boxes and this space was tightly packed with mineral wool, the inner box being well insulated in this manner. Across one corner of the inner box a board was nailed, this board was four inches shorter than the box and was nailed into the box so as to leave a clear space of two inches at the top and bottom of the box. The triangular space formed by this board and the corner of the box was lined with 1/4" asbestos board so as to insulate it. This space then formed a chimney and near the bottom of this chimney the electric lights used to heat the boxes were hung. The temperature was regulated by means of a mercury regulator which consisted of a large bulb of mercury expanding up a capillary tube. A platinum wire was fused into the bulb so as to be in contact with the mercury. Down the top of the capillary tube a long fine needle was placed so that when the

mercury was expanded to a certain height at a definite temperature the mercury would just come in contact with the needle. Wires were run from the regulator to a telegraph relay, the mercury regulator being connected in series with the regulator. The telegraph relay was used to make and break the 220 volt circuit on which the lights used for heating were connected.

The jars of coal were placed on several bricks in the inner box, the bricks being arranged so as to elevate the jar high enough so that it would be in the middle of the box and also to allow the air around the jar to circulate freely. The cover of the inner box was then put on the box and through holes in the latter several long thermometers (about 2 1/2 feet long) were placed so as to get the temperature of the air in the box and of the coal. The thermometers used to get the temperature of the air in the box were placed so that one was near the heating chimney and the other was at a point farthest from it. The thermometer used to get the temperature of the coal was placed so that the bulb was four or five inches below the surface of the coal. Readings of these temperatures were taken every morning and afternoon.

In the first run, called Series I, five sizes of the coal were used. These samples were not what would be known as air-dry because the coal was used as soon as it was ground, the large lumps however were air dry. The five sizes were as follows:-

Size 0. This size was some of the coal that went through the smallest holes in the screen and then was ground in a disk pulverizer so that it was very finely divided. About 75% of this size coal went through a 120 mesh screen and all of it went through an 80 mesh

Size 0-1/8. This was the coal that went through the 1/8" holes in the large revolving screen.

Size 1/8-1/4. This was the coal that went through the 1/4" holes in the screen.

Size 1/4-3/8. This was the coal that went through the 3/8" holes in the screen.

Size 3/8-3/4. This size was a mixture of equal parts of the coal that went through the 1/2" and 3/4" holes in the revolving screen, it was thought that there would not be enough difference between the results of the 1/2" size and the 3/4" size, so the two were mixed in equal proportions.

METHOD OF PROCEDURE.

A jar of each of the four largest sizes of coal was placed in the ovens in the same increasing ration of size of the coal and temperature of the oven, e.g. size 0-1/8 was put in the 40° oven, size 1/8-1/4 in the 60° oven, size 1/4-3/8 in the 80° oven, and size 3/8-3/4 in the 115° oven. This method of procedure was adopted so as to save time for by this means all the ovens could be filled at once and since it takes 12 days for a coal to pass through the four ovens a considerable saving of time resulted, also the large sizes of coal were not oxidized to an appreciable extent at these low temperatures. After the coals had remained in the ovens for three days they were moved up to the next oven, size 3/8-3/4 was taken out of the 115° oven and the next smaller size put in and size 0 was put in the 40° oven. The reading of the temperatures was made in the morning and afternoon chiefly to see that the regulators and lights

were working well, but also to get the increase in temperature of the coal over that of the ovens. As is shown on plate VI the maximum rise in temperature in some cases took place before the end of three days. This was especially the case in the finer sizes. The average temperatures of the ovens and the temperature of the coal at the end of the three days is found on the temperature tables of the various series at the end of the work.

Series II was identically the same as Series I, the only difference being that the coal in Series II was thoroughly wet before placing in the ovens.

Before beginning Series II, in order to get some idea as to the oxidation of the coal and the amount of oxygen used up by it, the air in the different ovens was analyzed, after the coal had been in the ovens for three days. The results were as follows:-

	Oven 1 40°	Oven 2 60°	Oven 3 80°	Oven 4 115°
% CO ₂	0.40	1.20	1.00	1.81
% Oxygen	20.00	18.40	19.40	16.00

Since the oxygen content decreased so much it was thought necessary to ventilate the ovens so as to maintain atmospheric conditions. This was done by boring several one half inch holes through the walls of both boxes near the bottom and putting a 1/2" glass tube through the two walls. One of the tubes was placed so that the fresh cool air that came in was delivered at the bottom of the heating chimney, and the other tube delivered its air at the opposite side of the box. At the top of the box a take-off pipe of the same size was inserted.

The coal used in these experiments had the following proximate analysis:-

	Size 0-1/8	Size 1/8-1/4
Moisture	4.16	4.62 %
Volatile matter	33.48	33.37 %
Fixed carbon	49.60	48.59 %
Ash	11.50	11.13 %
Sulphur	1.26	1.29 %

Calculated to Dry Coal.

Volatile matter	34.92	34.78 %
Fixed carbon	51.76	52.23 %
Ash	12.00	11.64 %
Sulphur	1.32	1.35 %

The pyritic iron was determined by taking the difference between the total iron in the coal and the iron soluble in hydrochloric acid. The results for the above two samples are as follows:-

Total iron	1.91	1.73 %
HCl soluble Fe	0.73	0.67 %
Pyritic iron	1.18	1.06 %
Calculated pyrite content	1.76	1.60 %

Seeing that more of the larger sizes were used than the finer, the average pyrite content of the coal was taken as 1.65%. In the following experiments in which the coal was made up to higher pyrite contents some large lumps of pyrite taken from a coal mine were used. This pyrite was ground so as to go through a 20 mesh sieve and was 87.62% pure, this being determined by finding the sulphur content which was 46.73% and calculating it to FeS_2 .

For Series III and IV the coal was made up to contain 3% pyrite. In Series IV the coal was thoroughly wet before placing in the ovens, otherwise it was the same as Series III.

For Series V the coal was made up to contain 5% of pyrite. In the last three series the two largest sizes were discarded for from the results of Series I and II it is seen that it was not worth while to run them, so in the last three series only sizes 0, 0-1/8, and 1/8-1/4 were used.

RESULTS.

The results of the five series as far as temperature increases are concerned are given in the five tables, pages 46 to 50. These temperature increases were also plotted in the form of curves in which the oven temperatures were plotted as the abscissae and the rise over the oven temperatures as the ordinates. These curves show many interesting results. From the curve of Series I, we simply see that the oxidation increases as the size of the coal decreases and that most of the oxidation - if it may be measured by the rise in temperature - takes place at a temperature higher than 60°C. From the curve of Series II, we see as may be expected that any heat generated by the process of oxidation is used in driving off the water with which the coal was thoroughly soaked before putting in the ovens. But at 80°C we get an increase in temperature over the oven temperature, even though the coal still contains some moisture. The final increase in temperature is, however, somewhat greater than in Series I, when the same coal was used dry. In the curve of Series III, something new and very interesting appears which, however, had been noticed in Series I, but had not been studied as closely, and this is the rate of oxidation. As is seen on the curve, size 0, is made up of two curves one of which rises to a temperature of 75.3°, and the other rises to a temperature of 46°, which is even lower than the final temperature of the next larger size which is 51.0°. Since this fact, - that the oxidation of the coal increases rather suddenly for a short time and then gradually decreases, - was discovered in the earlier series it was now studied in greater detail

in size 0 of Series III with the results shown in a graphical form on page As seen from this curve the coal saturates itself with oxygen about thirty hours after it is introduced in the oven and after this time the temperature gradually decreases until the final temperature is only about one-half the maximum temperature attained by the coal.

In Series IV, which was coal having the same pyrite content as the preceeding series only in this case the coal was first thoroughly wet, several new points are seen. Size $1/8-1/4$, which was as dust free as was possible to make it, dried out very soon and showed an increase in temperature even in the 40° and 60° ovens, whereas the two finer sizes did not even get dry at these temperatures. Size 0 at the end of three days showed an increase over the oven temperature of 113.7° , this being as high as the thermometers would register. On removal from the oven and on examination the following day it was found that the coal had taken fire and that the thermometer was not down far enough in the coal to measure the total increase in temperature. The coal took fire down in the middle of the jar and because of the slight access of air the burning was only a slow smoldering. The jar was left out in the room temperature for about two weeks after it was taken from the oven and was then re-examined and it was found that the coal on the interior of the jar had burned completely to an ash although there was a ring of unburned coal all around the inside of the jar about three inches thick. This ring of unburned coal probably acted as an insulator for the burning coal within the jar, for being at room temperature the coal nearest the sides of the jar was at too low a temperature to burn.

After removing size 0-1/8 from the ovens it was also allowed to stand for several weeks before removing the coal from it and it was found that it also had started to burn, although the combustion was not as complete as in the former case and although the rise in temperature while in the ovens was not any greater than some of the dry coals had attained and which had not taken fire under similar conditions. This series shows therefore the effect of having the coal wet and also shows how much more dangerous and how much greater is the liability of a coal to ignite spontaneously if it has been wet. The fact that the coal in this series took fire and that the coal in the preceeding series which was of the same composition, did not, shows the significance and danger arising from a coal dependant entirely upon the condition in which it is stored.

Series V shows a slightly greater degree of oxidation than does Series III, which might be expected from the fact that the former series contains 5% of pyrite and the latter only 3% of the same. The coal in Series V was dry, the same as in Series III. The increase in temperature of the coal over the oven temperatures for the lower ovens was practically the same for both series. So beyond the fact that the oxidation of this series with a higher pyrite content than the previous one was a little greater than in the other series, no other new facts were disclosed. The increase of oxidation of Series V over Series III does not seem to be very marked and so there is a possibility that this increase is not due to the greater pyrite content of the coal.

In order to find how great an oxidation of pyrite took place the water soluble sulphur in the fresh coal and the various

sizes of oxidized coal was determined. This was only done in Series II and IV where the coal had been wet for it was thought that the oxidation of the dry pyrite would not be very great. The results are as follows:-

Water soluble sulphur in the fresh coal 0.062 %

Water soluble sulphur in the oxidized coal in Series II.

Size 0	0-1/8	1/8-1/4	1/4-3/8	3/8-3/4
0.196%	0.178%	0.0317%	0.0231%	0.0214%

Water soluble in the oxidized coal in Series IV.

Size 0	0-1/8	1/8-1/4
0.340%	0.349%	0.1088%

Since the original coal as used in Series II contained 1.65% of pyrite and the coal in Series IV contained 3% of pyrite it is seen that the amount of pyritic oxidation was the same for both coals in the finer sizes, for in the first case the water soluble sulphur is 0.196% and in the second case it is 0.340% which numbers are very nearly in the same ratio as 1.65 and 3. In the larger sizes however this relation does not hold, for in size 1/8-1/4 the oxidation of Series IV is about one and one half times as great as in Series II.

CONCLUSIONS.

From the results of the experimental work different conclusions may be drawn but the following seem to be the most important and certain.

1. The finer sizes of coal oxidize more rapidly and with a greater increase in temperature than the larger sizes.
2. Coal oxidizes very quickly for a short time (the finer sizes especially) with a corresponding rise in temperature, then the coal seems to have saturated itself with oxygen and the subsequent oxidation is much slower and the temperature gradually decreases.
3. Wet coal is much more liable to ignite spontaneously, after drying, than dry coal even though the coals be of the same composition.
4. The addition of pyrite seems to cause a greater oxidation and also an increase in temperature, and seems to make the coal more liable to ignite, especially if the coal has been wet. If the coal is kept dry the increase in pyrite content does not seem to cause much of an increase in temperature.

SERIES I.

DRY COAL
1.65% Pyrite.

	Coal 0	Coal 0-1/8	Coal 1/8-1/4	Coal 1/4-3/8	Coal 3/8-3/4
Time in hours	96.0	89.0			
Oven Temperature °C.	38.8	40.0			
Coal " "	41.7	42.5			
Rise " "	2.9	2.5			
Time in hours	89.0	76.0	89.0		
Oven Temperature °C.	60.0	60.5	60.0		
Coal " "	65.0	63.7	63.5		
Rise " "	5.0	3.2	3.5		
Time in hours	77.0	74.0	76.0	89.0	
Oven Temperature °C.	80.0	80.0	79.8	77.0	
Coal " "	95.0	91.1	89.7	78.0	
Rise " "	15.0	11.1	9.9	1.0	
Time in hours	42.0				
Oven Temperature °C.	108.0				
Coal " "	168.0				
Rise " "	60.0				
Time in hours	72.0	89.0	74.0	76.0	89.0
Oven Temperature °C.	108.0	109.0	107.8	108.0	107.0
Coal " "	154.0	140.0	133.2	127.9	122.4
Rise " "	46.0	31.0	25.4	19.9	15.4

SERIES II.

WET COAL
1.65% Pyrite.

	Coal 0	Coal 0-1/8	Coal 1/8-1/4	Coal 1/4-3/8	Coal 3/8-3/4
Time in hours	72.0	81.0			
Oven Temperature °C.	38.5	38.5			
Coal " "	38.3	38.5			
Rise " "	----	----			
Time in hours	84.0	72.0	81.0		
Oven Temperature °C.	60.0	59.0	59.5		
Coal Temperature " "	57.5	58.5	62.4		
Rise " "	----	----	2.9		
Time in hours	72.0	84.0	72.0	81.0	
Oven Temperature °C.	80.0	80.0	80.0	80.0	
Coal " "	86.5	85.5	86.3	85.6	
Rise " "	6.5	5.5	6.3	5.6	
Time in hours	48.0				
Oven Temperature °C.	111.5				
Coal " "	168.3				
Rise " "	56.8				
Time in hours	72.0	72.0	84.0	72.0	81.0
Oven Temperature °C.	114.0	111.9	110.2	112.5	111.5
Coal " "	164.8	148.2	131.0	128.0	125.5
Rise " "	50.8	36.3	20.8	16.5	14.0

SERIES III.

DRY COAL
3% Pyrite.

	Coal 0	Coal 0-1/8	Coal 1/8-1/4
Time in hours	71.0	71.0	
Oven Temperature °C.	37.0	39.5	
Coal " "	42.0	42.0	
Rise " "	5.0	2.5	
Time in hours	72.0	71.0	71.0
Oven Temperature °C.	60.0	60.0	66.0
Coal " "	68.2	67.5	60.0
Rise " "	8.2	7.5	6.0
Time in hours	72.0*	72.0	71.0
Oven Temperature °C.	75.0	80.0	81.5
Coal " "	88.6	93.5	93.8
Rise " "	13.6	13.5	12.3
Time in hours	20.0		
Oven Temperature °C.	115.0		
Coal " "	190.3		
Rise " "	75.3		
Time in hours	72.0	72.0*	72.0
Oven Temperature °C.	115.0	114.0	114.0
Coal, " "	161.0	165.0	138.0
Rise " "	46.0	51.0	28.0

*The heat current had been turned off at power house. Coals were left two days longer.

SERIES IV.

WET COAL
3% Pyrite.

	Coal 0	Coal 0-1/8	Coal 1/8-1/4
Time in hours	72.0	72.0	72.0
Oven Temperature °C.	39.5	40.0	39.5
Coal " "	39.5	39.2	42.3
Rise " "	----	----	2.8
Time in hours	72.0	72.0	72.0
Oven Temperature °C.	60.0	60.0	61.0
Coal " "	56.5	55.7	66.5
Rise " "	----	----	5.5
Time in hours	72.0	72.0	72.0
Oven Temperature °C.	80.0	80.0	80.0
Coal " "	86.7	82.8	89.8
Rise " "	6.7	2.8	9.8
Time in hours	72.0	72.0	72.0
Oven Temperature °C.	112.5	115.0	115.0
Coal " "	226.2	172.0	126.0
Rise " "	113.7	57.0	11.0
	Coal took fire.	Coal took fire.	

SERIES V.

DRY COAL
5% Pyrite.

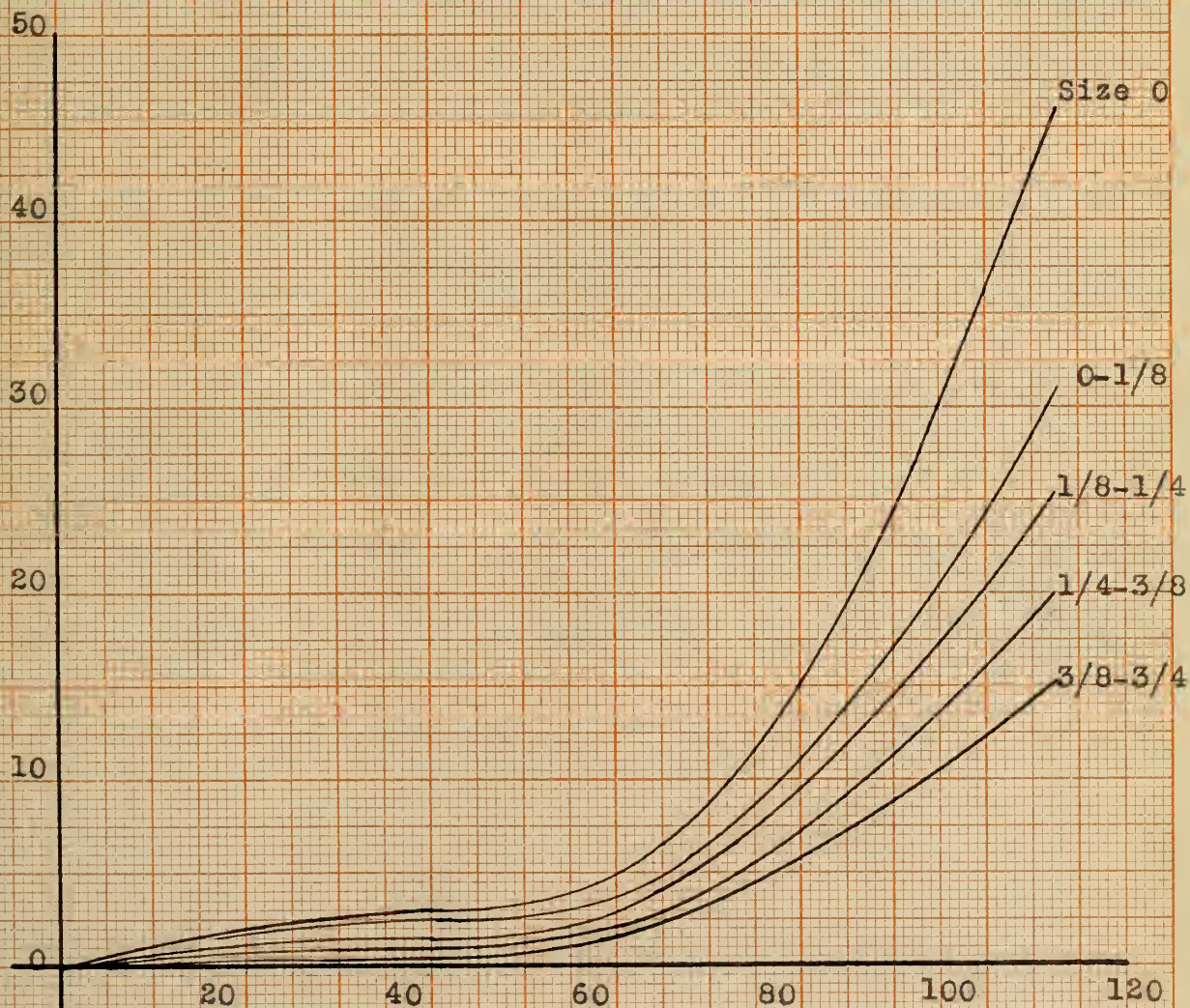
	Coal 0	Coal 0-1/8	Coal 1/8-1/4
Time in hours	72.0	72.0	72.0
Oven Temperature °C.	34.0	39.0	40.0
Coal " "	38.0	42.4	42.0
Rise " "	4.0	3.4	2.0
Time in hours	72.0	72.0	72.0
Oven Temperature °C.	60.5	60.3	61.0
Coal " "	70.0	66.2	66.6
Rise " "	9.5	5.9	5.6
Time in hours	*----	72.0	72.0
Oven Temperature °C.	"	80.5	81.0
Coal " "	"	88.2	89.2
Rise " "	"	7.7	8.2
Time in hours	72.0	72.0	72.0
Oven Temperature °C.	122.0	120.0	116.0
Coal " "	185.0	174.0	143.2
Rise " "	63.0	54.0	27.2

*Battery worn out, so regulator did not work, was recharged and put in order.

Plate 1. Showing the relation between the RISE IN TEMPERATURE
of the coal and the OVEN TEMPERATURE.

Series I, 1.65% Pyrite, Dry Coal.

Rise in
temperature
in degrees C.



Oven temperatures in degrees C.

Plate II. Showing the relation between the RISE IN TEMPERATURE of the coal and the OVEN TEMPERATURE.

Series II. 1.65% Pyrite. Wet Coal.

Rise in temperature in degrees C.

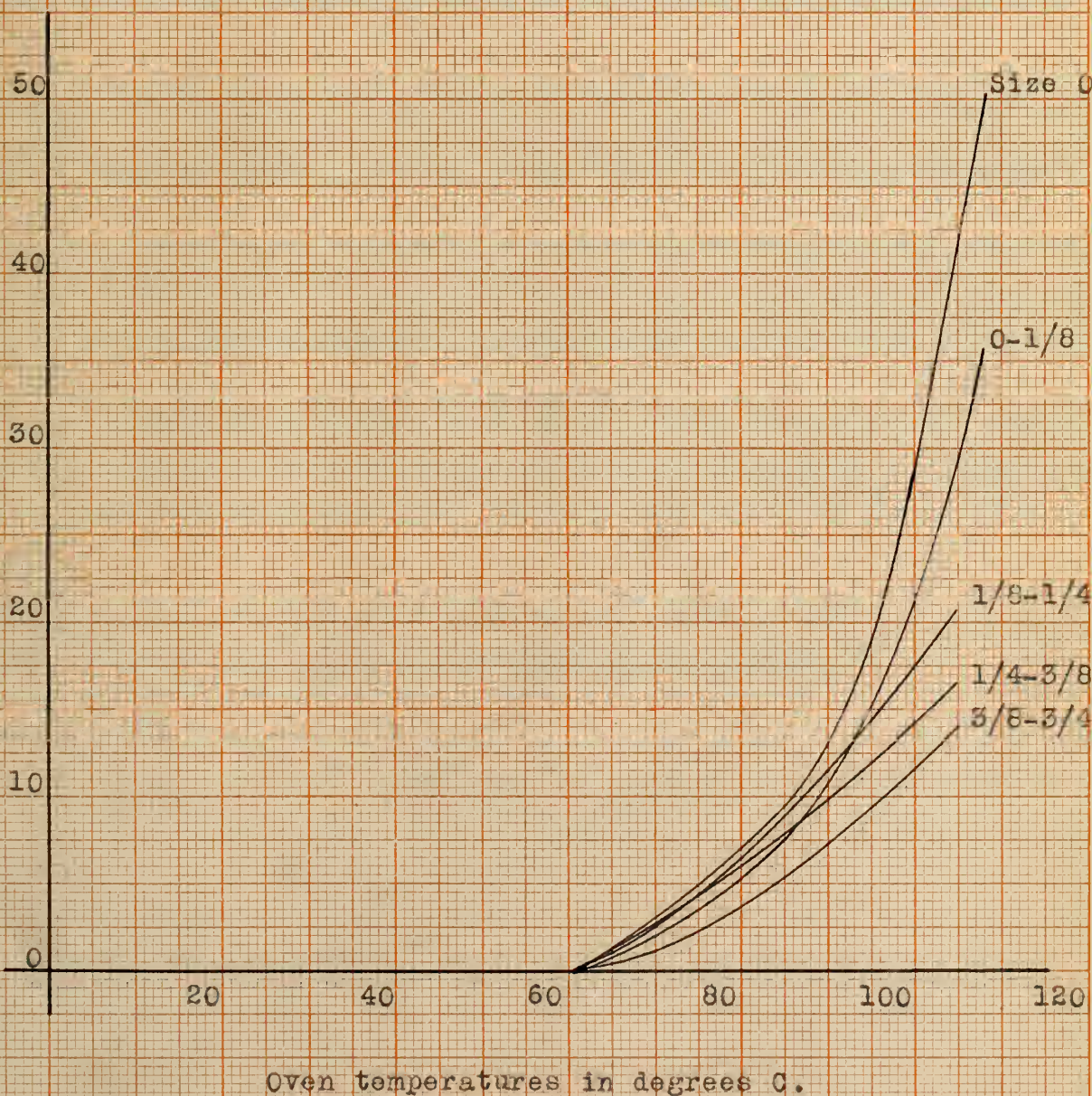
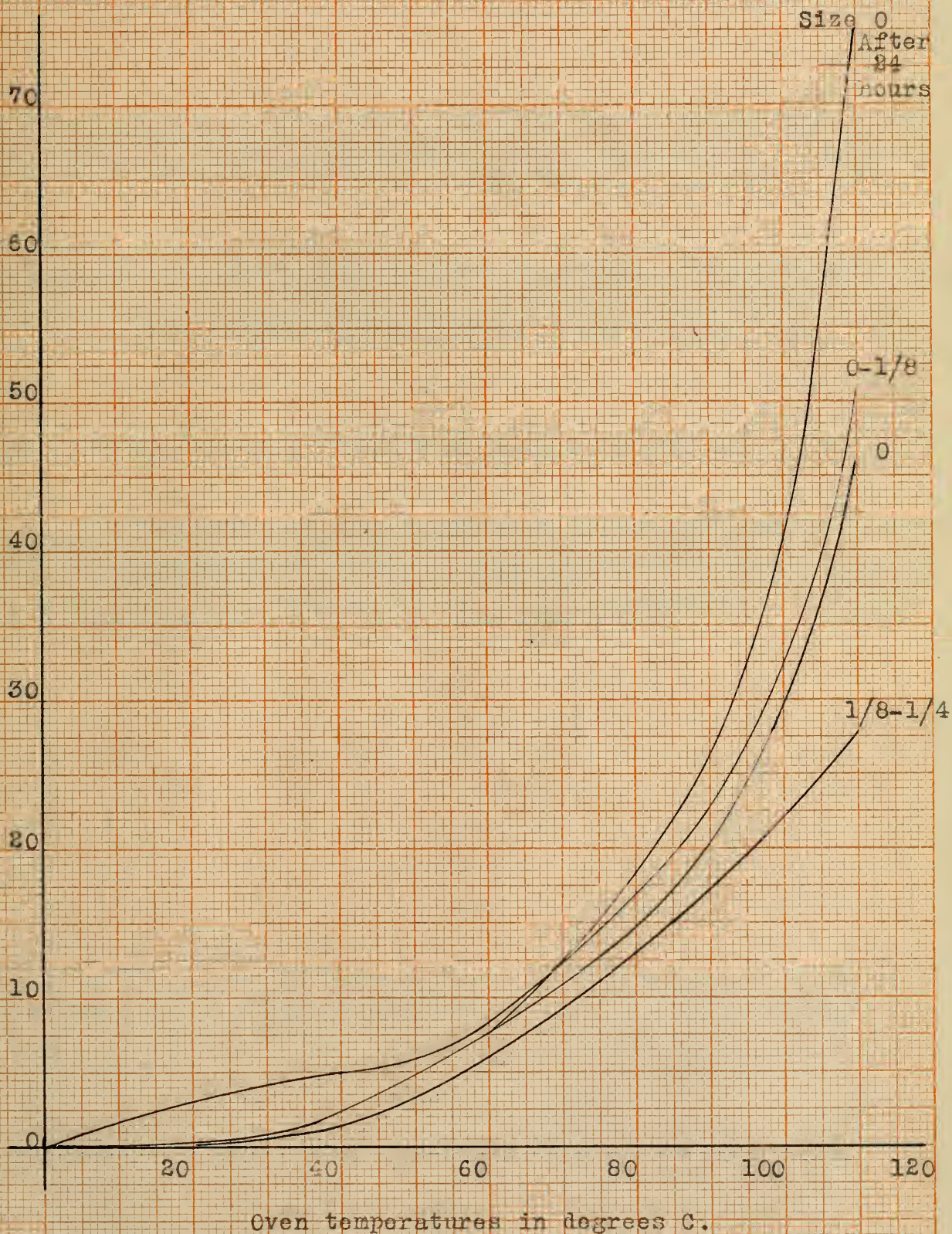


Plate III. Showing the relation between the RISE IN TEMPERATURE of the coal and the OVEN TEMPERATURE.

Series III. 3% Pyrite. Dry Coal.

Rise in temperature in degrees C.



Oven temperatures in degrees C.

Plate IV. Showing the relation between the RISE IN TEMPERATURE
of the coal and the OVEN TEMPERATURE.

Rise in Series IV. 3% Pyrite. Wet Coal.
temperature
in degrees C.

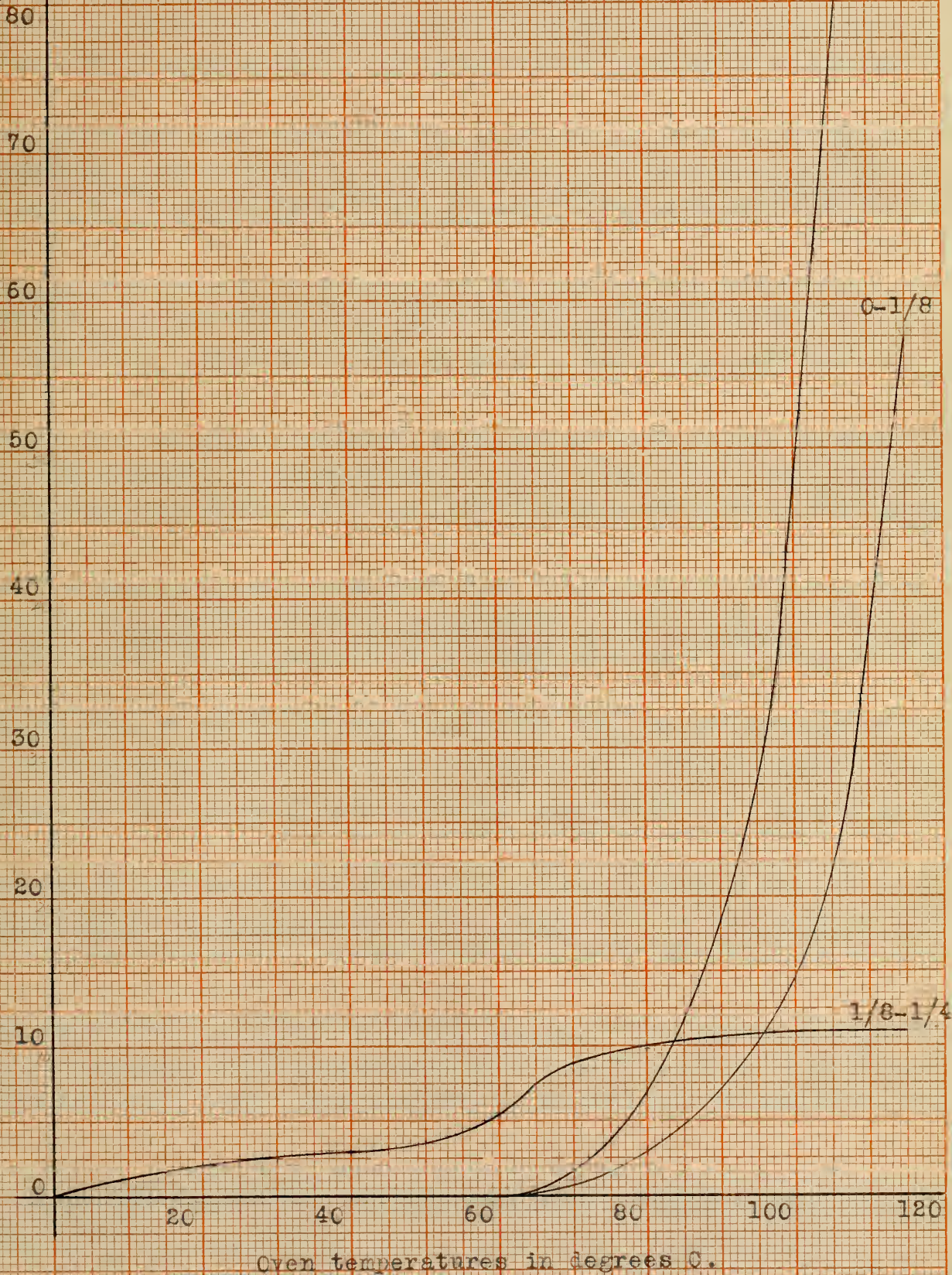


Plate V. Showing the relation between the RISE IN TEMPERATURE
of the coal and the OVEN TEMPERATURE.

Series V. 5% Pyrite. Dry Coal.

Rise in
temperature
in degrees C.

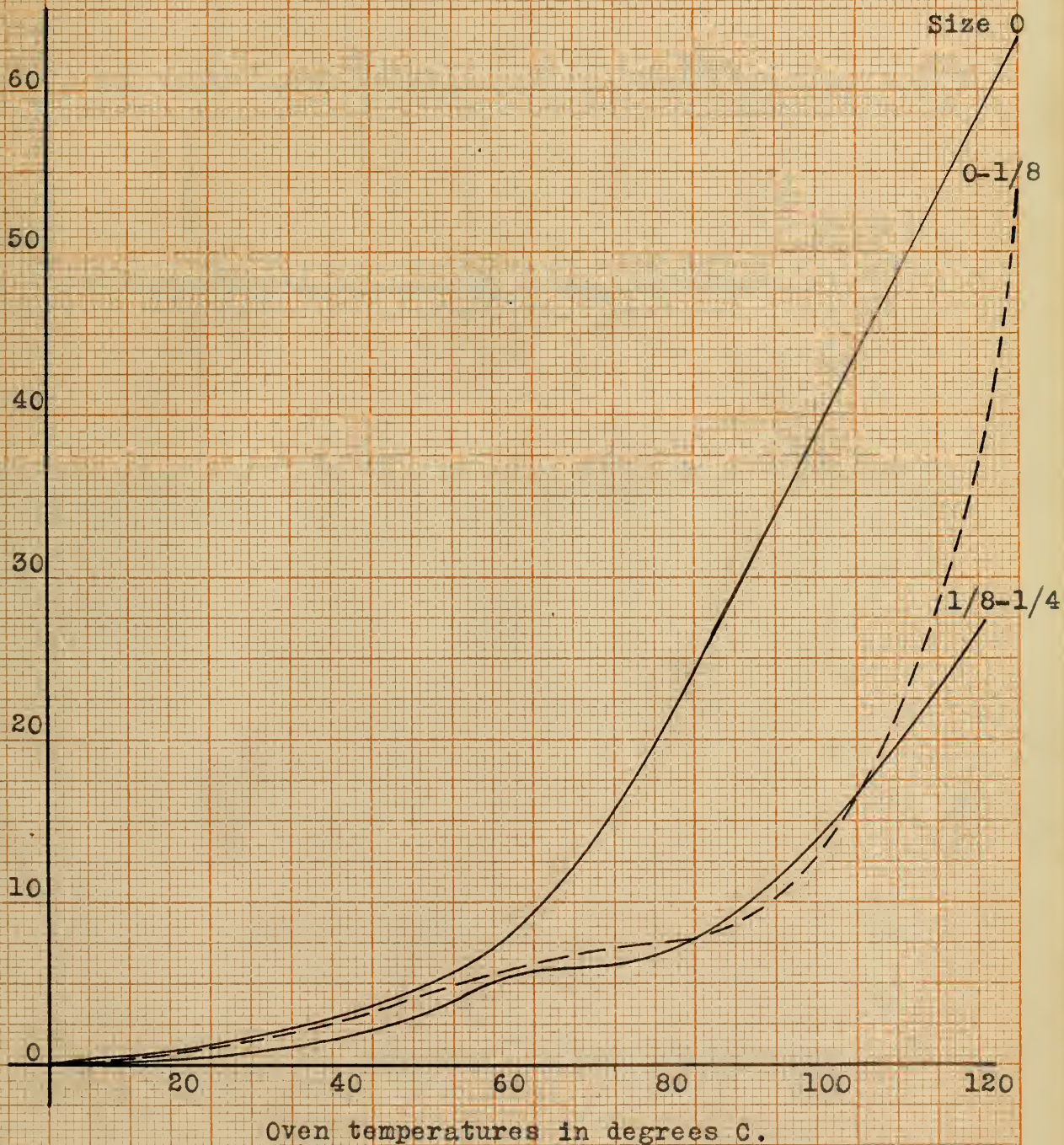


Plate VI. Showing the relation between the RISE IN TEMPERATURE of the coal and the TIME IN HOURS that it remains in the oven.

Coal size 0. Series III. 3% Pyrite. Dry Coal.

Increase in temp. over oven temp. in °C.

80°

60°

50°

40°

30°

20°

10°

0

20

40

60

80

Time in Hours.

Plate VII. Showing the relation between the WATER SOLUBLE SULPHUR (expressed in percent) and the SIZE OF THE COAL.

Series II. 1.65% Pyrite. Wet Coal.

Water Soluble
Sulphur in
Percent.

0.20

0.16

0.12

0.08

0.04

0

$1/8$

$1/4$

$3/8$

$1/2$

$3/4$

Size of Coal.

Plate VIII. Showing the relation between the WATER SOLUBLE SULPHUR (expressed in percent) and the SIZE OF THE COAL.

Series IV. 3% Pyrite. Wet Coal.

Water Soluble Sulphur in Percent.

0.35

0.30

0.25

0.20

0.15

0.10

0.05

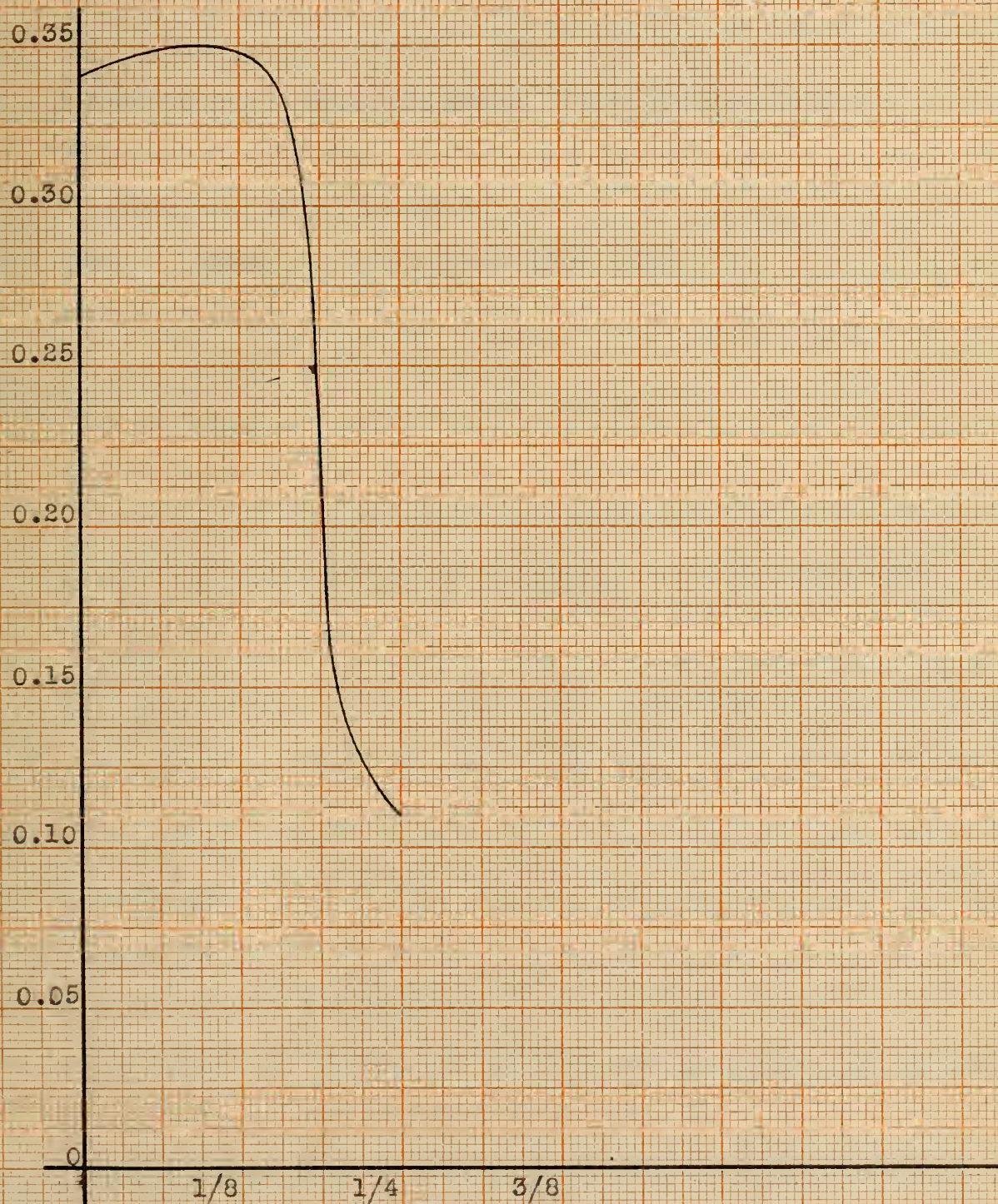
0

1/8

1/4

3/8

Size of Coal.



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